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(54) **PROCESS FOR COLORING POLYMER.**

(57) A process for coloring polymers, which comprises the steps of: dipping a polymer which swells in water or an aqueous solvent mixture or a molding of the polymer in a treating fluid comprising an aqueous solvent mixture containing a colorant having an affinity for the polymer to thereby swell the polymer and at the same time impregnate the colorant into the polymer, and dipping the polymer thus treated in water, an aqueous acid solution or an aqueous solution of an oxidizing agent to fix the colorant to mold, it is possible to carry out swelling and mold release simultaneously.

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TECHNICAL FIELD

The present invention relates to a process for coloring a polymer product. The present invention also relates to a process for coloring a molded article of a polymer product which is partly in contact with a mold while releasing the molded article from the mold.

The present invention is preferably applied to the coloring of not only a contact lens, particularly a soft contact lens, but also to a variety of polymer products or molded articles other than contact lenses such as films, membranes, etc., formed from hydrogels.

TECHNICAL BACKGROUND

Conventional processes for dyeing hydrogel resin articles are described in JP-A-53-13673 and JP-A-53-128667. These processes are both based on the premise that a hydrogel resin article is brought into a fully swollen state by means of water, a solvent which is more capable of swelling a hydrogen resin article than water and compatible with water, or a mixed solvent of water and said solvent. That is, a hydrogel resin article is dyed as follows: After a hydrogel resin article is fully swollen, the hydrogel resin article is infiltrated with a water-soluble dye or a leuco or colorless compound thereof, and subjected to water-insolubilization and color-forming treatments.

In the processes proposed in the above two Publications, in short, the step of swelling a polymer product to be dyed, and the step of infiltrating a water-soluble dye or a leuco or colorless compound thereof into the swollen polymer product are isolated from each other as a separate step. For this reason, the above processes have had a problem in that the infiltration of the dye into the swollen polymer product is liable to be nonuniform and it is difficult to dye a number of polymer products in a uniform dyed state.

The present invention has been made to overcome the above problem. It is a first object of the present invention to provide a process for coloring a polymer product, according to which a large quantity of polymer products can be colored uniformly with a decrease in the number of steps.

It is a second object of the present invention to provide a process for coloring a molded article of a polymer product being partly in contact with a mold while releasing the molded articles from molds, according to which a large quantity of molded articles can be colored uniformly with a decrease in the number of steps.

DISCLOSURE OF THE INVENTION

The present invention has been made to achieve the above objects. The process for coloring a polymer product by which to achieve the first object comprises;

a step of immersing a polymer product, which is swellable in water or a water-containing mixed solvent, in a treating liquid comprising a water-containing mixed solvent containing a colorant having affinity to said polymer product thereby to carry out the swelling of said polymer product and the infiltration of the above colorant into said polymer product at the same time, and

a step of immersing the above polymer product treated in the above step, in water, an acidic aqueous solution or an aqueous solution of an oxidizing agent thereby to fix the above colorant.

The process for coloring a molded article by which to achieve the second object comprises;

a step of immersing a molded article being formed of a polymer product which is swellable in water or a water-containing mixed solvent and being partly in contact with a mold, in a treating liquid comprising a water-containing mixed solvent containing a colorant having affinity to said molded article thereby to carry out the releasing of said molded article from the mold, the swelling of said molded article and the infiltration of the above colorant into said molded article at the same time, and

a step of immersing the above molded article treated in the above step, in water, an acidic aqueous solution or an aqueous solution of an oxidizing agent thereby to fix the above colorant.

MOST PREFERRED EMBODIMENTS FOR WORKING THE INVENTION

In the process for coloring a polymer product, provided by the present invention to achieve the first object, the polymer product to be colored is limited to those which can swell in water or a water-containing mixed solvent. Such polymer products include products produced from materials such as a hydroxyethyl methacrylate (HEMA) polymer, an N-methylpyrrolidone (NVP) polymer, an N-vinylpyrrolidone (NVP)-methyl methacrylate (MMA) copolymer, an HEMA-MMA-methacrylic acid (MA) copolymer, a copolymer composed mainly of HEMA and NVP, a glycerol methacrylate-MMA copolymer, polyvinyl alcohol, polyacrylamide, a polyacrylamide derivative, etc. The form of the polymer product is not specially limited. The polymer product includes those which are amorphous such as powders and those which have predetermined forms. In particular, contact lens molded articles, are preferred as a polymer product.

In addition, the polymer product to be colored may be a polymer product or a molded article

which has been immersed in a sodium hydrogencarbonate aqueous solution, subjected to heat treatment and then treated to bring it into an equilibrium hydrous state in a physiological saline solution or a contact lens preservation liquid (a buffer solution of which the pH and osmotic pressure are adjusted) (this treatment is referred to as "equilibrium hydration treatment" hereinafter), or it may be a molded product or a molded article which has not been subjected to the equilibrium hydration treatment. For example, when the polymer product is a contact lens, the polymer product may be any molded product having a contact lens form which is obtained by a method in which raw material monomer(s) is (are) directly (co)-polymerized in a mold (spin cast method and mold cast method), or by a method in which raw material monomer(s) is (are) (co)polymerized in any one of various polymerization reactors and the resultant product is cut and polished. The polymer product may also be a dry contact lens which has not yet been subjected to any equilibrium hydration treatment or a hydrous contact lens which has been subjected to the equilibrium hydration treatment. Further, it may be a colorless and transparent, hydrous soft contact lens which is commercially available.

In the process for coloring a polymer product, provided by the present invention, first, there is carried out a step in which the above polymer product is immersed in a treating liquid comprising a water-containing mixed solvent containing a colorant having affinity to the polymer product. As a colorant, any colorant may be used if it has affinity to a polymer product to be colored. Generally preferred are solubilized vat dyes such as Red 1, Blue 1, 2 or 6, Brown 1, Black 1, etc., and vat dyes such as Blue 1, 3, 4 or 5, Green 1, 3, 13 or 45, Orange 3, 5 or 13, etc. The colorant can be properly selected depending upon the kind of a polymer product to be colored and a color to be applied to the polymer product.

The water-containing mixed solvent is preferably selected from those which are obtained by mixing water with organic solvents: Examples of the organic solvents are alcohols such as methanol, ethanol, isopropanol, n-butanol, etc.; ketones such as acetone, methyl ethyl ketone, etc.; glycols such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, etc.; or the like. The above colorant is added to this water-containing mixed solvent, whereby there is obtained a treating liquid in which the colorant is homogeneously dissolved in the water-containing mixed solvent.

The reason for the use of a water-containing mixed solvent as a solvent to dissolve the colorant is as follows. By increasing the swelling ratio of the polymer product, the pore diameter of the polymer product is enlarged up to a size suitable for coloring, and the treating liquid in which the colorant is dissolved is rapidly infiltrated into the whole of the polymer product, whereby the polymer product is uniformly colored.

The use of water alone as a solvent has a problem in that the treating liquid in which the colorant is dissolved is hardly infiltrated due to a small swelling ratio of the polymer product and a small pore diameter of the polymer product. The use of an organic solvent alone has a problem in that it is difficult to dissolve the colorant up to a concentration necessary for the coloring since the solubility of the colorant in the organic solvent is low.

In the water-containing mixed solvent, the water/organic solvent mixing ratio is preferably 20:80 to 80:20. The reason therefor is that when the content of water is greater than this range, the polymer product sometimes has a small swelling ratio and an insufficient pore diameter, and that when the content of the organic solvent is greater, the solubility of the colorant in the mixed solvent is sometimes insufficient. When a vat dye is used, however, it is preferred to add a reducing agent, etc., to the water-containing mixed solvent in order to dissolve the colorant in the water-containing mixed solvent uniformly. The reason for adding the reducing agent is that since a vat dye is a water-insoluble dye, the vat dye is converted to a water-soluble leuco compound with the reducing agent. As a reducing agent, preferred is, for example, hydrosulfite ($Na_2S_2O_4$), or the like.

When the above polymer product is immersed in the treating liquid comprising a water-containing solvent containing a colorant, the polymer product is swollen, and the colorant is uniformly infiltrated into the polymer product.

The water-containing mixed solvent may contain, for example, sodium nitrite, sodium sulfite, etc., in order to proceed with the color-forming reaction rapidly. The amount thereof for use is preferably 0.5 to 2 % by weight. Further, the water-containing mixed solvent may contain, for example, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium chloride, sodium sulfate, etc., in order to increase the stability of the treating liquid. The amount thereof for use is preferably 0.5 to 2 % by weight.

In the process for coloring a polymer product, provided by the present invention, there is then carried out a step in which the swollen polymer product obtained in the above step and infiltrated with the colorant is immersed in water, an acidic aqueous solution or an aqueous solution of an oxidizing agent. The acidic aqueous solution or the aqueous solution of an oxidizing agent used in this step is selected from aqueous solutions of acetic

acid, sulfuric acid, nitric acid, hydrochloric acid, hypochlorous acid, boric acid, etc. When the polymer product is immersed in water, the acidic aqueous solution or the aqueous solution of an oxidizing agent, the colorant in the polymer product is fixed to give a uniformly colored polymer product.

When the polymer product is a contact lens, the contact lens, which has been subjected to the above fixing treatment, is immersed in a sodium hydrogencarbonate aqueous solution, heat-treated, and brought into an equilibrium hydrous state in a physiological saline solution or a contact lens preservation liquid (buffer solution of which the pH and osmotic pressure are adjusted), whereby there is obtained a colored hydrous soft contact lens.

The process for coloring a molded article, provided by the present invention to achieve the second object, will be explained below. The process for coloring a molded article, provided by the present invention, differs from the above process for coloring a polymer product only in that the article to be colored is a molded article being formed of a polymer product which is swellable in water or a water-containing mixed solvent and being partly in contact with a mold. Therefore, only this difference is detailed, and the explanation of the other points is omitted.

In the process for coloring a molded article, provided by the present invention, the article to be colored is a molded article formed of a polymer product which is swellable in water or the water-containing mixed solvent and being partly in contact (usually in tight contact) with a mold. Such a molded article includes a contact lens material obtained by a so-called single-sided cast method in which a monomer is cast into an open-top cylindrical polymerization reactor (also called a single-sided casting mold) and heat- or photopolymerized. The resultant contact lens material is in a state in which it is tightly in contact with the bottom of the mold. As this mold, preferred is a mold which has a bottom of a curved surface for forming a convex or concave surface of a soft contact lens and is formed from a plastic material such as polyethylene, polypropylene, polycarbonate, polysulfone, etc. The reason therefor is that the above contact lens material obtained by the polymerization can be formed into a contact lens by cutting and polishing the molded article together with the mold while the molded article is tightly in contact with the bottom of the mold. The mold is also partially cut off due to the cutting and polishing, and the molded article having a contact lens form is tightly in contact with the bottom of the mold. After the cutting and polishing, the molded article having a contact lens form and being tightly in contact with the bottom of the mold is immersed in the treating liquid comprising a water-containing mixed solvent containing a colorant having affinity to said molded article, whereby the molded article is swollen and the colorant is infiltrated into the molded article, and the release of the molded article from the mold occurs.

Thereafter, similarly to the former process for coloring a polymer product, the molded article is immersed in water, an acidic aqueous solution or an aqueous solution of an oxidizing agent, whereby the colorant is fixed to give a uniformly colored molded article. In addition, after the fixing treatment, the molded article having a contact lens form is consecutively immersed in an aqueous sodium hydrogencarbonate solution, heat-treated and immersed in a physiological saline solution or a contact lens preservation liquid to give a colored hydrous soft contact lens, which procedure and result are the same as those in the above process for coloring a polymer product.

According to the process for coloring a polymer product and the process for coloring a molded article, provided by the present invention, swelling a polymer product or a molded article and infiltrating a colorant into the polymer product or the molded article are carried out at the same time as specified above. Therefore, not only the procedure is simplified as compared with the afore-described processes of prior arts in which they are carried out separately, but also there is produced a remarkable effect that a colorant is uniformly infiltrated into the polymer product or the molded article. Therefore, a number of polymer products and molded articles can be colored in a uniform colored state with a decrease in the number of steps, and the present invention has great industrial significance.

The present invention will be further detailed by reference to Examples.

Example 1

A commercially available, colorless and transparent soft contact lens formed from hydroxyethyl methacrylate (HEMA) as a main monomer component (trade name: HOYA SOFT) was immersed in a treating liquid containing a colorant and a water-containing mixed solvent (consisting of 0.03 part by weight of solubilized vat dye Blue 6, 50 parts by weight of distilled water, 50 parts by weight of reagent special-grade ethanol, 0.5 part by weight of reagent special-grade sodium hydrogencarbonate and 0.5 part by weight of reagent special-grade sodium sulfite) for 75 minutes to swell the soft contact lens and, at the same time, to infiltrate the colorant into the soft contact lens. At this stage, the soft contact lens was colored yellow or yellowish brown.

Then, the colorant was fixed by immersing the

soft contact lens in an aqueous solution containing 1 % by weight of sulfuric acid to give a blue-colored soft contact lens.

The colored contact lens was immersed in an aqueous solution containing 1 % by weight of sodium hydrogencarbonate for 75 minutes, and then the aqueous solution containing 1 % by weight of sodium hydrogencarbonate was replaced with a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate to immerse the colored soft contact lens in the new aqueous solution for 75 minutes. The colored contact was taken out of the aqueous solution containing 1 % by weight of sodium hydrogencarbonate, and transferred into a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate. The colored contact lens was heated therein at 80° C for 90 minutes, and heated in a physiological saline solution at 80° C for 90 minutes twice to give a blue-colored hydrous soft contact lens.

The above-obtained colored hydrous soft contact lens was sectioned, and its cross section was optically magnified and observed with an optical microscope to show the coloring of the soft contact lens deep into its central portion uniformly and no change in the lens form.

Comparative Example 1

Commercially available contact lens formed from HEMA as a main monomer component (trade name: HOYA SOFT) was immersed in a mixed solvent containing 50 parts by weight of distilled water and 50 parts by weight of ethanol for 75 minutes to swell the soft contact lens. Thereafter, the soft contact lens was immersed in a coloring liquid containing 0.03 part by weight of a solubilized vat dye Blue 6 and 100 parts by weight of distilled water for 75 minutes. An excess amount of the colorant adhering to the lens surface was washed away with distilled water, and the contact lens was immersed in a solution consisting of an aqueous solution containing 0.5 % by weight of sodium nitrite and an aqueous solution containing 1 % by weight of sulfuric acid, and then treated in an aqueous solution containing 1 % by weight of sodium hydrogencarbonate. Thereafter, the contact lens was treated in the same manner as in Example 1 to give a blue-colored hydrous soft contact lens. In this process, the contact lens was colored, but when the contact lens was washed with distilled water, the removal of the colorant by washing was nonuniform, and the contact lens showed no stability in the final color density. Further, when the contact lens was washed by immersing it in distilled water for a predetermined period of time, the diffusion of the colorant occurred from the interior of the contact lens.

Example 2

99.8 Parts by weight of HEMA, 0.2 part by weight of ethylene glycol dimethacrylate (to be abbreviated as EGDMA hereinafter) and 0.2 part by weight, per 100 parts by weight of the monomer mixed solution in total, of 2,2'-azobis-(2,4-dimethylvaleronitrile) (to be abbreviated as V-65 hereinafter) as a polymerization initiator were mixed, and mutually dissolved. Then, this mixture solution was cast into a mold, and the mold was closed and kept in a hot air-circulating dryer at 40° C for 25 hours. And, the temperature in the hot air circulating dryer was increased up to 45° C over 15 hours, increased from 45° C to 60° C over 10 hours, increased from 60° C to 80° C over 8 hours, and increased from 80° C to 100° C over 4 hours, and the mold was kept at 100° C for 8 hours to finish the polymerization. Then, the temperature was reduced to room temperature, and the resultant copolymer was taken out of the mold. The resultant colorless transparent rigid polymer was cut and polished by an ordinary processing technique to shape the copolymer into a contact lens form.

Then, this lens in a rigid state was immersed in the same treating liquid as that used in Example 1 for 75 minutes to swell the lens and at the same time to infiltrate the colorant into the lens. At this stage, the lens was colored yellow or yellowish brown.

The above lens was immersed in an aqueous solution containing 1 % by weight of sulfuric acid for 75 minutes. The lens was shrunk from the swelling state to show a blue coloring.

The above colored lens was immersed in an aqueous solution containing 1 % by weight of sodium hydrogencarbonate for 75 minutes, and the aqueous solution containing 1 % by weight of sodium hydrogencarbonate was replaced with a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate to immerse the colored lens in the fresh aqueous solution for 75 minutes. In this state, the lens was in a swollen state nearly equivalent to the swollen state of a hydrous soft contact lens according to the final product standard, and the lens had strength sufficient to handle it with a pair of tweezers (or pincette) or by fingers. The colored contact lens was taken out of the sodium hydrogencarbonate aqueous solution, and transferred into a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate, heated at 80° C for 90 minutes, and it was further heated in a physiological saline solution at 80° C for 90 minutes twice to give a blue-colored hydrous soft contact lens.

When this colored hydrous soft contact lens was heated in boiling water for 100 hours, no change in coloring occurred. Further, this soft con-

tact lens passed the elution test based on the contact lens acceptance standard published by Ministry of Health and Welfare.

The above colored soft contact lens was sectioned, and its cross section was optically magnified and observed with an optical microscope to show that the soft contact lens was uniformly colored deep into its central portion without unevenness.

Comparative Example 2

The same monomer mixed solution as that used in Example 2 was polymerized in the same manner as in Example 2, and the resultant copolymer was cut and polished in the same manner as in Example 2 to shape it into a contact lens form. Then, the resultant lens was immersed in a mixed solvent containing 50 parts by weight of distilled water and 50 parts by weight of ethanol for 75 minutes to swell it. Then, the lens was immersed in a coloring solution containing 0.03 part by weight of a solubilized vat dye Blue 6 and 100 parts by weight of distilled water for 75 minutes. An excess amount of the colorant adhering to the lens surface was washed away with distilled water, and the contact lens was immersed in a solution consisting of an aqueous solution containing 0.5 % by weight of sodium sulfite and an aqueous solution containing 1 % by weight of sulfuric acid, and treated in an aqueous solution containing 1 % by weight of sodium hydrogencarbonate. Thereafter, the contact lens was treated in the same manner as in Example 2 to give a blue-colored hydrous soft contact lens. In this process, the contact lens was colored, but when the contact lens was washed with distilled water, the removal of the colorant by washing was nonuniform, and the contact lens showed no stability in the final color density. Further, when the contact lens was washed by immersing it in distilled water for a predetermined period of time, the diffusion of the colorant occurred from the interior of the contact lens.

Example 3

A soft contact lens material formed from HEMA as a main monomer component, which had been obtained by the polymerization in an open-top cylindrical polymerization container (single-sided casting mold) having a bottom with a curvature corresponding to a base curve (inner surface curve) of the contact lens and being formed from a plastic material, was cut and polished in the front curve (outer surface curve) while it was tightly in contact with the single-sided casting mold, whereby there was obtained a contact lens of which the base curve was tightly in contact with the bottom of the single-sided casting mold. Then, the single-sided casting mold with the contact lens tightly in contact with it was placed in a beaker, and the same treating liquid as that used in Example 1 was poured in the beaker. The single-sided casting mold was immersed in the treating liquid for 75 minutes to release the contact lens from the single-sided casting mold and at the same time to carry out the swelling of the lens and the infiltration of the colorant into the lens. The contact lens released from the single-sided casting mold was colored yellow or yellowish brown. The above treating liquid was discharged from the beaker. An aqueous solution containing 1 % by weight of sulfuric acid was newly poured into the beaker, and the contact lens was immersed therein for 75 minutes. The contact lens was shrunk from its swollen state to show the coloring of blue. Then, the aqueous solution containing 1 % by weight of sulfuric acid was discharged, and an aqueous solution containing 1 % by weight of sodium hydrogencarbonate was poured in the beaker, in which the contact lens was immersed for 75 minutes. Thereafter, this solution was replaced with a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate, and the contact lens was immersed in this sodium hydrogencarbonate aqueous solution for 75 minutes. In this state, the contact lens was in a swollen state nearly equivalent to the final product standard, and the lens had strength sufficient to handle it with a pair of tweezers or by fingers. The solution had weak alkalinity of pH of 7 to 8, and the aqueous solution containing 1 % by weight of sulfuric acid was neutralized. The lens was taken out of the beaker, and transferred into a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate. The lens was heated at 80° C for 90 minutes, and then heated in a physiological saline solution at 80° C for 90 minutes twice to give a blue-colored hydrous contact lens.

When this colored hydrous soft contact lens was heated in boiling water for 100 hours, no change in coloring occurred. Further, this soft contact lens passed the elution test based on the contact lens acceptance standard published by Ministry of Health and Welfare.

The above colored soft contact lens was sectioned, and its cross section was optically magnified and observed with an optical microscope to show that the soft contact lens was uniformly colored deep into its central portion without unevenness.

This Example has shown that the release of the lens from the mold and the infiltration of the colorant take place at the same time, and the lens is uniformly colored, since the lens is in a state in which it is released from the mold and swollen, and the colorant is brought into an equilibrium state in

which it is infiltrated deep into the lens central portion.

Example 4

A colored soft contact lens was prepared in the same manner as in Example 3 except that a polishing material remained adhering to the contact lens surface after the cutting and polishing of the front curve (outer surface curve). Portions of the lens surface to which the polishing material was adhering did not show any nonuniformity in the coloring. This Example has shown that the colorant infiltrates into the lens concurrently with the swelling of the lens, nonuniformity in the coloring due to a foreign matter adhering to the lens surface is not caused.

Example 5

A soft contact lens material formed from N-vinylpyrrolidone (NVP) as a main component and obtained by the polymerization in a single-sided casting mold was cut and polished in the front curve while it was tightly in contact with the single-sided casting mold to give a contact lens of which the base curve was tightly in contact with the bottom of the single-sided casting mold. The single-sided casting mold with the contact lens tightly in contact with it was placed in a beaker. Then a treating liquid containing a colorant and water-containing mixed solvent (consisting of 0.06 part by weight of a solubilized vat dye Red 1, 40 parts by weight of distilled water, 60 parts by weight of reagent special-grade isopropanol and 0.5 part by weight of reagent special-grade potassium hydrogencarbonate) was poured in the beaker, in which the single-sided casting mold with the contact lens was immersed for 60 minutes, whereby the contact lens was released from the single-sided casting mold and at the same time, the swelling of the lens and the infiltration of the colorant into the lens were completed. The above treating liquid was discharged from the beaker, and an aqueous solution containing 5 % by weight of acetic acid was newly poured to immerse the contact lens therein for 75 minutes. The contact lens was shrunk from the swelling state to show the coloring of red. Then, the above solution was replaced with an aqueous solution containing 1 % by weight of sodium hydrogencarbonate, and the contact lens was immersed therein for 75 minutes. The lens was taken out of the beaker, transferred into a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate, and heated at 80° C for 90 minutes. Further, the lens was heated in a physiological saline solution at 80° C for 90 minutes twice to give a red-colored soft contact lens. The colored state thereof was as excellent as that in Example 3.

Example 6

A soft contact lens material obtained by the polymerization in a single-sided casting mold and formed mainly from N-vinylpyrrolidone (NVP), methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), was cut and polished in the front curve while it was tightly in contact with the single-sided casting mold to give a contact lens of which the base curve was tightly in contact with the bottom of the single-sided casting mold. The single-sided casting mold with the contact lens tightly in contact with it was placed in a beaker. Then a treating liquid containing a colorant and water-containing mixed solvent (consisting of 0.06 part by weight of a solubilized vat dye Green 1, 20 parts by weight of distilled water, 80 parts by weight of reagent special-grade acetone, 0.5 part by weight of reagent special-grade sodium nitrite and 0.5 part by weight of reagent special-grade sodium hydrogencarbonate) was poured in the beaker, in which the single-sided casting mold with the contact lens was immersed for 90 minutes, whereby the contact lens was released from the single-sided casting mold and at the same time, the swelling of the lens and the infiltration of the colorant into the lens were completed. The above treating liquid was discharged from the beaker, and an aqueous solution containing 1 % by weight of nitric acid was newly poured to immerse the contact lens therein for 90 minutes. The contact lens was shrunk from the swelling state to show the coloring of green. Then, the above solution was replaced with an aqueous solution containing 1 % by weight of sodium hydrogencarbonate, and the contact lens was immersed therein for 90 minutes. The lens was taken out of the beaker, transferred into a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate, and heated at 80° C for 90 minutes. Further, the lens was heated in a physiological saline solution at 80° C for 90 minutes twice to give a green-colored soft contact lens. The colored state thereof was as excellent as that in Example 3.

Example 7

A soft contact lens material formed from hydroxyethyl methacrylate (HEMA) as a main component and obtained by the polymerization in a single-sided casting mold was cut and polished in the front curve while it was tightly in contact with the single-sided casting mold to give a contact lens of which the base curve was tightly in contact with the bottom of the single-sided casting mold. The single-sided casting mold with the contact lens

tightly in contact with it was placed in a beaker. Then a treating liquid containing a colorant and water-containing mixed solvent (consisting of 0.03 part by weight of a solubilized vat dye Black 1, 50 parts by weight of distilled water, 50 parts by weight of reagent special-grade ethyl alcohol, 0.5 part by weight of reagent special-grade sodium nitrite and 0.5 part by weight of reagent special-grade potassium hydrogencarbonate) was poured in the beaker, in which the single-sided casting mold with the contact lens was immersed for 90 minutes, whereby the contact lens was released from the single-sided casting mold and at the same time, the swelling of the lens and the infiltration of the colorant into the lens were completed. The above treating liquid was discharged from the beaker, and the above solution was replaced with a fresh aqueous solution containing 0.1 % by weight of hypochlorous acid to immerse the contact lens therein for 60 minutes. The lens was taken out of the beaker, transferred into a fresh aqueous solution containing 1 % by weight of sodium hydrogencarbonate and heated at 80° C for 90 minutes. Further, the lens was heated in a physiological saline solution at 80° C for 90 minutes twice to give a black-colored soft contact lens. The colored state thereof was as excellent as that in Example 3.

As specified above, according to the present invention, polymer products or molded articles can be colored uniformly and in a large quantity. Further, since the number of the production steps can be decreased, the production efficiency can be improved remarkably. In particular, the present invention is very useful for coloring soft contact lenses obtained by a single-sided casting method.

Claims

1. A process for coloring a polymer product, which comprises;

   a step of immersing a polymer product, which is swellable in water or a water-containing mixed solvent, in a treating liquid comprising a water-containing mixed solvent containing a colorant having affinity to said polymer product thereby to carry out the swelling of said polymer product and the infiltration of the above colorant into said polymer product at the same time, and

   a step of immersing the above polymer product treated in the above step, in water, an acidic aqueous solution or an aqueous solution of an oxidizing agent thereby to fix the above colorant.

2. A process according to claim 1, wherein the polymer product is formed from a material selected from the group consisting of a hydroxyethyl methacrylate (HEMA) polymer, an N-methylpyrrolidone (NMP) polymer, an N-vinylpyrrolidone (NVP)-methyl methacrylate (MMA) copolymer, an HEMA-MMA-methacrylic acid (MA) copolymer, a copolymer formed from HEMA and NVP as a main component, a glycerol methacrylate-MMA copolymer, polyvinyl alcohol, polyacrylamide and polyacrylamide derivative.

3. A process according to claim 1 or 2, wherein the polymer product is a contact lens molded article.

4. A process according to claim 1, wherein the water-containing mixed solvent is a mixture of water with at least one organic solvent selected from the group consisting of alcohols, ketones and glycols.

5. A process according to claim 1, wherein the colorant is a solubilized vat dye or a vat dye.

6. A process according to claim 1, wherein the acidic aqueous solution or the aqueous solution of an oxidizing agent is an aqueous solution of a compound selected from acetic acid, sulfuric acid, nitric acid, hydrochloric acid, hypochlorous acid and boric acid.

7. A colored polymer product obtained by the process for coloring a polymer product, recited in any one of claims 1 to 6.

8. A process for coloring a molded article which comprises;

   a step of immersing a molded article being formed of a polymer product which is swellable in water or a water-containing mixed solvent and being partly in contact with a mold, in a treating liquid comprising a water-containing mixed solvent containing a colorant having affinity to said molded article thereby to carry out the releasing of said molded article from the mold, the swelling of said molded article and the infiltration of the above colorant into said molded article at the same time, and

   a step of immersing the above molded article treated in the above step, in water, an acidic aqueous solution or an aqueous solution of an oxidizing agent thereby to fix the above colorant.

9. A process according to claim 8, wherein the molded article is formed from material selected from the group consisting of a hydroxyethyl methacrylate (HEMA) polymer, an N-methylpyrrolidone (NMP) polymer, an N-vinylpyr-

rolidone (NVP)-methyl methacrylate (MMA) copolymer, an HEMA-MMA-methacrylic acid (MA) copolymer, a copolymer formed from HEMA and NVP as a main component, a glycerol methacrylate-MMA copolymer, polyvinyl alcohol, polyacrylamide and polyacrylamide derivative.

10. A process according to claim 8 or 9, wherein the molded article is a contact lens molded article.

11. A process according to claim 8, wherein the water-containing mixed solvent is a mixture of water with at least one organic solvent selected from the group consisting of alcohols, ketones and glycols.

12. A process according to claim 8, wherein the colorant is a solubilized vat dye or a vat dye.

13. A process according to claim 8, wherein the acidic aqueous solution or the aqueous solution of an oxidizing agent is an aqueous solution of a compound selected from acetic acid, sulfuric acid, nitric acid, hydrochloric acid, hypochlorous acid and boric acid.

14. A colored molded article obtained by the process for coloring a molded article, recited in any one of claims 8 to 13.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/00422

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl[5] D06P3/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	D06P3/00, G02C7/04

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	JP, A, 58-104286 (Ricky Contact Lens Research Institute Inc.), June 21, 1983 (21. 06. 83) & US, A, 4,494,954	1-14
X	JP, A, 53-128667 (Toppan Printing Co., Ltd.), November 9, 1978 (09. 11. 78) & DE, A1, 2728613	1-14
X	JP, A, 53-114876 (Toppan Printing Co., Ltd.), October 6, 1978 (06. 10. 78) & GB, A, 1583492	1-14
X	JP, A, 53-13673 (Toppan Printing Co., Ltd.), February 7, 1978 (07. 02. 78), (Family: none)	1-14

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
May 10, 1991 (10. 05. 91)	May 20, 1991 (20. 05. 91)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	